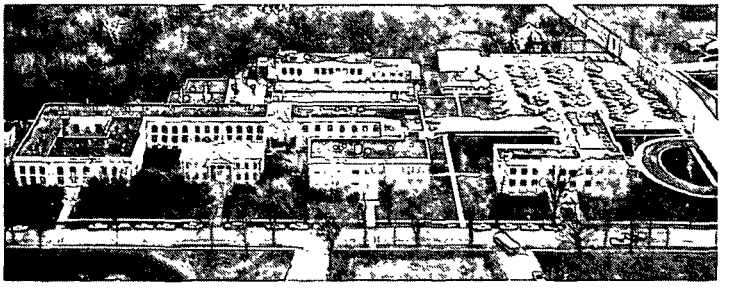

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

IPC TECHNICAL PAPER SERIES
NUMBER 247

CHEMICAL RECOVERY TECHNOLOGY — A REVIEW

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JULY, 1987

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This paper was prepared at the request of TAPPI and is to be presented at the CHINA PAPER 87 Conference in Shanghai on October 14-15, 1987

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ABSTRACT A comprehensive review of the state of the art of chemical recovery technology is made with a particular focus on recovery for small mills and for nonwood pulping. Kraft recovery technology is the most advanced, but is not generally suited to small nonwood pulping operations. Sulfite recovery technology is also generally too complex for these types of operations. Sulfur-free soda pulping would provide the best opportunity for relatively simple recovery technologies. The DARS process may provide a very attractive chemical recovery system for the small soda mill. Its applicability to nonwood pulping depends on the behavior of silica in the combustion step. There remains a need for a simple and reliable method for desilicating black liquor. This is the key to effective recovery for alkaline nonwood pulping. Continued development of biological processes may provide some longer range solutions for small nonwood pulping chemical recovery.

Introduction

Chemical recovery systems are essential elements of chemical pulping processes. Recovery directly reduces chemical costs. The organic substances in the spent liquor can serve as a fuel source to meet part of the energy requirements of the mill. The destruction of the organic material and the return of the pulping chemicals minimizes the environmental impact of the pulp mill. The recovery systems can be as costly as the pulping operation itself.

This paper is concerned with a comprehensive review of the state of the art of chemical recovery technology. It will begin with kraft chemical recovery from the pulping of wood, since this is the dominant method by which chemical pulp is produced in the world today. In addition, the paper will focus on recovery for small mills and for nonwood pulping, since this is most relevant to the present and short term future condition of the Chinese pulp and paper industry. The influence of large amounts of silica on recovery operations is a major consideration.

The paper considers kraft recovery, soda recovery and sulfite recovery in turn. Certain operations (pulp washing, evaporation, combustion, and chemical processing) which are common to most recovery technologies are dealt with as appropriate. Special problems with these operations in nonwood pulping recovery are considered separately. Methods for removing silica from the system are then considered. The review ends with consideration of biological techniques that might have application to recovery, especially when dealing with high yield pulping processes.

Kraft Recovery

The active pulping chemicals in the kraft process are sodium sulfide and caustic (sodium hydroxide). When the liquor is burned under reductive conditions in a recovery boiler the sodium and sulfur which are present in the black liquor are converted to sodium carbonate and sodium sulfide. An aqueous solution of these chemicals, called green liquor, can be causticized with lime (calcium oxide) to regenerate the pulping chemicals. The calcium carbonate formed during causticizing may be recovered and reburned to form lime. The distinguishing feature of the kraft process is the presence of sulfide in the pulping liquor. The kraft pulping and recovery process has proven to be especially adaptable to producing quality pulp from a wide variety of wood species. The trend has been toward very large scale operations with mill production rates in excess of 300,000 tpy. Existing mills represent a very large capital investment, and so most of the developments in kraft recovery technology have focused on improvements and optimization of the existing technology rather than on major innovations.

Pulp washing

The standard method for pulp washing in the kraft industry remains the drum washer (also called the rotary vacuum washer). This device consists of a cloth-covered cylinder rotating in a vat containing pulp. A pulp mat is formed on the surface of the cylinder and dewatered with the aid of a vacuum maintained inside the cylinder. On the upper part of the cylinder, where the pulp mat is not immersed in the vat, wash water is applied with showers. Several of these types of washers are usually arranged in series with counterflow of pulp and wash liquor.

A modification of the drum washer system is the pressure washer. This is also a rotary drum device, but the dewatering of the pulp mat is done with the aid of pressure applied inside the washer hood and outside the cylinder. Up to three separate showering stages operating countercurrently can be incorporated.

Where Kamyr continuous digesters are used, a substantial amount of washing is usually carried out within the digester following the cooking zone, and the black liquor is drawn directly from the extraction screens on the digester. A single drum washer stage following the continuous digester is usually adequate, with the filtrate from the drum washer used as wash water for the continuous digester.

Kamyr diffusion washers are sometimes used instead of drum washers. In these units the pulp flows upward through annuli formed by concentric double-sided screen rings. Wash liquor is introduced through distributors located in the annuli and forced to flow through the pulp to the screens where it is extracted. The screens move up along with the pulp and then periodically move downward to wipe the pulp from the screens and prevent plugging. Although the system is mechanically complex, it has proven to be an effective washing system on wood pulp.

Kraft washing systems are capable of giving sodium recovery efficiencies of 98% with dilution factors between 2 to 3. Recovered liquor concentrations are usually about 14% solids. This is considered satisfactory.

Evaporation

In the past the standard method of concentrating kraft black liquor was a multiple effect LTV (long tube vertical) evaporator set producing liquor at about 50%

solids, followed by a direct contact evaporator to raise the solids content to about 65% for firing into the furnace. This is no longer the case.

The most significant change has been the replacement of the direct contact evaporator with the concentrator (an indirect heated evaporator that produces liquor at firing concentrations). Although difficulties were experienced with the first generation of concentrator systems during the early 1970's, this technology has improved to the point where it is now standard to produce 70% solids liquor in concentrators, with no major difficulties. The most popular design, particularly in newer installations, appears to be the HPD crystallizer-evaporator system. In this approach the liquor is heated in forced circulation heat exchangers and then flashed in a crystallizing chamber. Large recirculation rates provide good heat transfer rates and avoid fouling of the heaters. Another successful design is the Rosenblad plate-type falling film unit. In this device liquor flows down the outside of a rectangular heater surface. Large recirculation rates are employed to give adequate velocities and to minimize the concentration change occurring along the hot surface.

One of the current thrusts is toward higher solids contents. With reasonably behaved liquors, new concentrator systems are capable of producing liquor at 70% solids or higher. Several mills have reported operating at over 70%. Very recently a superconcentrator installation in Finland was reported to be operating commercially at 80% solids and a second mill was reported to be at 76%. There are gains in energy efficiency and in recovery boiler throughput attainable with these very high solids levels. Perhaps dry black liquor solids will soon be fired in recovery boilers.

Falling film evaporators have some significant advantages over LTV evaporators and are beginning to make inroads. The falling film evaporator has a

much greater turndown capacity than an LTV and can operate with much smaller temperature differences as thermal driving forces. In addition to the operating flexibility this provides, falling film evaporators can be combined into more effects than can LTVs. This can give better steam economy.

Evaporator scaling is not generally a major problem with kraft black liquors from pulping wood. Concentrators operate beyond the solubility limit of some of the black liquor inorganics, but are designed and operated to maintain these materials as suspended crystallites. No special precautions or steps need to be taken to deal with scaling problems.

During the late 70's and early 80's, considerable development went into waste heat pre-evaporators and vapor recompression evaporators, and some units were commercialized. With current energy costs, these activities have lost much of their thrust.

Freeze concentration as an alternative to evaporation for kraft black liquor has been examined and underwent some development. Sufficient information was developed to allow an economic analysis. This gave unfavorable results, and the development effort has been shelved.

Membrane processes are not being used for concentrating weak black liquor, although this has been examined periodically. Lack of selectivity, high membrane costs, and short membrane lifetimes have been the major stumbling blocks.

Burning of black liquor

The standard method for burning kraft black liquor remains the recovery boiler. Although there have been some changes in details, the recovery boiler remains

basically the same piece of equipment it has been over the last 30-40 years. Trends toward larger units and higher operating pressures continue. Energy recovery efficiencies have improved primarily because of the elimination of the direct contact evaporator and its replacement by the extended long flow economizer. Changes that have taken place over the last few years have been mainly toward improving the operability and optimizing the performance.

Composite tubes, with an outer layer of austenitic stainless steel, have become the material of choice for the lower furnace, since this gives much greater protection against corrosion. There remains considerable interest in finding lower cost alternatives. All-welded, membrane wall construction is now standard, although details vary with the manufacturer. The single drum recovery boiler is now operating successfully on a commercial scale. This may have long range impact on reducing erection costs and on allowing the steam generating section to be built in a manner less susceptible to plugging.

There is considerable variety and innovation with regard to air and liquor supplies to the boiler. Three levels of air introduction to the furnace are becoming accepted as standard, although the details (port locations and size, velocities, dampering, etc.), particularly at the secondary and tertiary levels, vary considerably. Automatic air port rodders are being used in a few mills with success. Liquor spray technology is also changing. Spraying on the wall and the old CE conical nozzle appear to be losing favor to stationary or partially stationary firing using modified nozzles.

At the present time there is great activity in renovating and retrofitting existing recovery boilers. The main reason is a desire to increase the liquor burning capacity of existing units. It appears that in the near future

most of the expansion of kraft pulping will take place at existing mills and that most of this will involve retrofits rather than new boiler construction.

Computerized control systems for the recovery boiler are slowly becoming accepted. There remains a great deal of inertia and some reluctance. Sensors are available for most input needs, although sensor maintenance continues to be a problem. Swedish control technology, now being marketed under the name of BLRBOMASTER, appears to be the most advanced system currently available. Television camera systems for viewing the bed have come into widespread use and have met with great acceptance by the operators.

There is a continuing concern with the vulnerability of the recovery boiler to explosions and extended, unplanned outages. Insurability is an issue. It is generally recognized that there is little likelihood that the vulnerability can be reduced through hardware changes alone and that human error is at the root of most serious incidents.

Causticizing

The basic process used for causticizing green liquor has changed very little over the years. The standard causticizing system employs gravity settlers (clarifiers) for removing impurities from the green liquor and the calcium carbonate (lime mud) from the causticized product. A slaker-classifier is used for initiating the causticizing reaction which is completed in a series of stirred-tank reactors. Lime mud is washed by dilution and thickening in a clarifier and dewatered by a rotary vacuum filter.

The major hardware change in the causticizing area has been the use of pressure filters to replace clarifiers, particularly for separating lime mud

from the product liquor. At least two types of units, very similar in construction, have been used commercially. The principle advantages are cleaner and hotter product liquor, compact installation, and low energy requirements. The pressure filter tends to be more sensitive to unreacted lime in the white liquor slurry. Pressurized causticizing systems to allow causticizing at higher temperatures have been introduced but have not yet been widely accepted.

Substantial improvements in the performance of the causticizing system have been obtained through better control of the operation. Advanced control technologies employing both feedforward and feedback techniques are now available and are becoming accepted. The most sophisticated systems employ on-line conductivity measurements to monitor the degree of conversion within the causticizers.

Calcining

The lime kiln is still the dominant method for reburning lime. Although the fluidized bed calciner has been in existence over 20 years, it has not supplanted the kiln. The main advantage of the fluid bed calciner, better energy efficiency, no longer exists. Lime kilns are now capable of operating at the same or lower fuel requirements.

Major improvements in the thermal efficiency of lime kilns have been made over the last 20 years. These include the use of product coolers, better insulation, heavier chain sections, and more effective dewatering of the lime mud feed. The most effective kilns are now capable of operating with a fuel demand of about 6.5 million Btu/ton lime (about 6 gJ/ton). Efforts have also gone into fueling kilns with alternate fuels such as wood waste, coal and petroleum coke.

In-process environmental control

Large kraft mills can have a major effect on the environment and there is much effort devoted to controlling emissions within the process. High efficiency electrostatic precipitators and scrubbers on the recovery stack and the lime kiln have essentially eliminated significant dust emissions. Collection and incineration of noncondensable gases within the process is now being implemented at many mills for odor control. Condensates can be stripped and the odorous gases incinerated. There now exist several kraft mills which are almost totally odorless.

Bleach plant effluents are not generally handled within the kraft recovery cycle unless they are free of chlorine. Effluents from oxygen or oxygen extraction stages have been handled by introducing them into the kraft liquor system.

Alternate kraft technologies

Research and development efforts to find an alternative to the kraft recovery system continue. At the present time, these are focusing on black liquor gasifiers to replace the expensive recovery boiler. A gasifier processes the black liquor to yield a combustible gas stream which could be used as a fuel and to convert the inorganic chemicals to a form suitable for regeneration and reuse. Two types of gasifier of interest are the slagging cyclone gasifier and the molten salt gasifier. The cyclone gasifier underwent considerable development in Sweden as the NSP process. Although that effort now seems to be shelved, modifications of that technology could still lead to an effective process. A current development is Rockwell International's molten salt gasification process. This uses a pressurized molten salt reactor to produce a kraft smelt along with a combustible

gas that could be cleaned and used as fuel in a gas turbine for combined cycle power generation. This appears to be a more complicated technology than the existing recovery boiler, but it could give a much more favorable electrical power/steam balance. Considerable development work is required before this technology would be commercially available.

Status of kraft recovery

Kraft recovery technology is mature and very capital intensive. Economic factors have driven the industry toward very large scale operations. Most recent developments have been aimed at operating improvements and small gains in efficiency. There is desire for some means, compatible with the existing process, which would give a 10-20% incremental capacity increase, but no generally accepted process to do this has materialized. Vulnerability issues have become important. Since the vulnerability increases with size, this may serve as a brake on the trend toward larger scales of operation. A major breakthrough that will lead to a simple, cheap, kraft recovery technology seems unlikely. The breakthrough, when it comes, will be a different pulping process combined with a recovery technology.

Soda Recovery

This covers the recovery technology for all sulfur-free, sodium-base alkaline pulping processes including any combination of sodium hydroxide and sodium carbonate along with organic substances, oxygen, etc. The chemistry of soda recovery is straightforward. Combustion of the black liquor converts the sodium compounds to sodium carbonate. Sodium hydroxide can be produced by causticizing the carbonate solution with lime. Alternative techniques, to be described later, exist in which the chemistry is slightly more complicated.

The major elements of soda recovery are similar to kraft. After being washed from the pulp the liquor is concentrated by evaporation and burned. Causticizing and calcining of the green liquor may follow if caustic is desired. Normally washers and evaporators are similar to those used for kraft but there may be some differences. With high-yield wood pulps or when agricultural residues are used, press washers or other special devices may be needed to effectively remove the liquor from the pulp. Soda liquors can be more prone to scaling (a severe problem with agricultural residues), and this may force the use of evaporator types that are more resistant to scaling or lower the extent to which the liquors can be concentrated. Combustion of soda liquors can take on different forms than that used for kraft. Since sulfide is not needed, there is no need to maintain a local reducing environment in the combustion step. Soda liquor combustion can be carried out in equipment such as fluidized beds that are not suitable for kraft. Most of the variations in soda recovery technology are connected with the combustion step. Causticizing and calcining, where practiced, is similar to kraft. High amounts of silica may make lime reburning impossible, and in that case causticizing is followed by mud disposal.

Smelter furnaces

Combustion of soda liquor can be carried out in smelter furnaces in which the combustion temperature is above the melting point of the sodium carbonate product and the smelt collects on the hearth and is drained off through spouts. The smelter may have water-cooled walls like a kraft recovery boiler or be of simpler construction with refractory brick walls. Soda liquor burns differently than kraft liquor and the smelt can be more viscous and difficult to drain. Some modifications in firing techniques and additives (e.g., potassium) to

improve smelt drainage characteristics may be necessary to successfully operate. Bed burning of soda liquor is very slow, and there is normally only a minimal char bed.

Combustion of liquor in waterwalled furnaces requires feed liquor solids levels above about 55%. The walls tend to cool the flame, and stable combustion can only be supported if the internal evaporative load is minimized. Thus the waterwalled smelter furnace is normally only used with an effective set of evaporators in a configuration where steam and power generation is maximized.

Simpler types of refractory lined smelters, such as a Broby furnace, can also be used. These give less overall energy recovery but have lower installation costs and are more suitable for small mills. The refractory lined smelter is used where evaporation is difficult. Firing solids contents can be lower, since heat is not absorbed by the walls to the same extent. Simple smelters are often used in conjunction with a direct contact evaporator (odors are not a problem with soda liquors). The direct contact evaporator makes some use of the heat content of the combustion gases and is not as prone to scaling and fouling problems. This approach is especially attractive for liquor containing large amounts of silica, since it avoids boiler surface that could slag and also provides for concentration of liquor very prone to fouling.

Fluidized bed combustion

Soda liquors have been successfully burned in fluidized beds. The combustion is carried out below the melting temperature and the sodium carbonate product forms the bed material. Most of the experience with this approach has been with corrugating medium mills which converted from neutral sulfite semichemical pulp (NSSC) to sulfur-free semichemical pulp. Fluidized bed incineration of NSSC

liquors was widely used, and the units were available. The sulfur-free liquor proved to be more difficult to burn autogenously because of a tendency for more volatile gas production which burned in the freeboard zone above the bed, but these difficulties have been overcome.

A major advantage for fluidized bed incineration is that the liquors only need to be concentrated to 35-40% solids before introduction into the fluidized bed. The evaporation of the water in the liquor helps to maintain combustion temperatures below the slagging temperature. This is attractive with liquors which are difficult to evaporate.

A major problem with fluidized bed incineration is sensitivity to impurities. The combustion temperature has to be at least about 700°C in order to burn up the carbon, and higher temperatures give better operation. The temperature cannot approach the melting temperature, or slagging and defluidization of the bed can occur. Substances that form low melting eutectics, such as chloride or potassium, can cause defluidization. Experience has shown that fluidized beds have low tolerance for chlorides.

Most of the original fluidized beds operated as so-called bubbling beds. These are known to be susceptible to defluidization. The evolving trend in fluidized bed combustion of coal for power generation is to use entrained beds where the gas velocity is much higher and the solid phase is carried over with the gas, separated by high temperature cyclones, and returned to the combustion chamber. The Ahlstrom Pyroflow system is an example of this type of unit. Entrained bed reactor systems could extend the use of fluidized bed incineration to slag prone liquors.

Wet combustion

The organic material in the liquor can be burnt in aqueous solution by reacting with air at suitable pressure and temperature. This wet combustion process, known as the Zimpro process, is used commercially in a few cases. The major advantage of the approach is that it avoids evaporation of the liquor (or at least minimizes it). This saves energy, equipment and avoids evaporator scaling problems. The disadvantage is that the process must take place in a high pressure reactor. The unit at Ontonagon, Michigan operates at about 315°C and 2800 psig. The liquor must be indirectly heated, and there is a substantial power requirement to compress the combustion air to reactor pressure. Low pressure steam generators and expansion turbines on the off-gas are used to meet some of the process energy demands. The overall result is a complex, capital intensive process.

Autocausticizing

Self causticizing (autocausticizing) systems are a recent development that appears very promising for soda recovery. An amphoteric metal oxide is present during combustion which can react with the sodium carbonate and drive off CO_2. The product, when reacted with water, then forms caustic and liberates the metal oxide which can be recycled. The chemistry of autocausticizing can be represented as follows:

$$Na_2CO_3 + n\ M_xO_y = Na_2O*(M_xO_y)n + CO_2$$

$$Na_2O*(M_xO_y)n + H_2O = 2\ NaOH + n\ M_xO_y$$

There are many amphoteric metal oxides which participate in such reactions, but the greatest interest has centered around ferric oxide, Fe_2O_3. The Fe_2O_3-based

system that has been developed and implemented commercially is known as DARS for Direct Alkali Recovery System.

In the DARS process black liquor is burned with particles of ferric oxide in a fluidized bed combuster forming sodium ferrite by the following reaction:

$$Na_2CO_3 + Fe_2O_3 = Na_2Fe_2O_4 + CO_2$$

The ferrite product is then leached with hot water to form caustic and ferric oxide according to the reaction:

$$Na_2Fe_2O_4 + H_2O = 2\ NaOH + Fe_2O_3$$

Coarse particles (1-3 mm) are maintained to allow more efficient dewatering of the ferric oxide after leaching. The fluid bed is a "bubbling bed" type combuster to minimize particle size reduction which would occur with a "circulating bed". The DARS fluidized bed is able to operate autogenously (with no auxiliary fuel) when firing liquors as low as 40% solids. The minimum solids content depends on the heating value of the liquor. Causticities up to 94% have been reported.

The DARS process was patented by Toyo Pulp Co. Ltd. of Japan in 1976. Process improvements involving the use of fluidized bed combustion and cold leaching for impurity removal were patented by Amcor Ltd. of Australia in 1980. The license for commercial development is held by Babcock and Wilcox of U.S.A. The first commercial plant has just gone into operation at the APPM mill in Burnie, Tasmania. This will process the liquor from 200 o.d. t/day of soda-AQ pulp from eucalyptus. The recovery system will process 320 t/d of liquor solids, producing 95 t/d of sodium hydroxide.

The DARS process shows promise of providing a simpler recovery technology that is suitable for smaller scale mills. Although it is still relatively unproven commercially, extensive development and pilot testing have been carried out over many years. One drawback to the process is that it is not applicable to kraft recovery because the iron oxide is reduced under the conditions needed to form sulfide.

An autocausticizing system that is workable with the kraft process is one based on borates. Borate autocausticizing has undergone development and mill scale testing in Finland, but the results of the mill test have never been published. One disadvantage to the borate process is that the inorganic combustion product is soluble in water, so that the oxide is not precipitated for recycle to the combustion stage. This means that the pulping must be carried out with the borate solution, which is not as alkaline as caustic. There is also a very high load of inorganic chemicals around the entire pulping and recovery cycle due to the recirculating autocausticizing agent.

Sulfite Recovery

The chemistry of sulfite recovery is a little more complicated than that for soda or kraft. The active chemical, sulfite, is in an intermediate oxidation state and is not produced directly by the combustion of the liquor under either oxidizing or reducing conditions. This results in generally more complex recovery systems. There is also much more variety, since sulfite pulping can be carried out over the full pH range and any of four different bases, sodium, magnesium, ammonium and calcium might be used.

Sodium-base systems

Sodium-base systems are of the greatest interest because they can be operated over the full pH range, especially at the neutral and alkaline end. They have been used for high-yield semichemical pulps and form the basis for some CMP processes. NSAQ and ASAQ pulping also involve sodium-base sulfite recovery.

Full oxidation of sodium/sulfur containing liquors produces sodium sulfate. This is a dead-end as far as regeneration of sulfite is concerned, and so complete oxidation must be avoided. Sulfite recovery for sodium-base systems has to be based on either reductive burning to form a sulfide smelt (as in the kraft furnace) and subsequent treatment to make the sulfite, or separation of sulfur from the sodium during combustion and subsequent recombination of SO_2 with sodium carbonate. All of these approaches are in use commercially. No single technology has shown enough advantage to dominate sodium-base sulfite recovery.

Recovery systems for reductive burning have a front end similar to the kraft system (washers, evaporators and a smelter furnace), although there are some differences. Sulfite liquors burn differently, and appropriate adjustments in firing techniques must be made. There is also a higher ratio of sulfur to sodium in the liquor than is common with kraft, and so there is a greater tendency toward high SO_2 levels in the flue gas. With high-yield pulping processes, the liquor may be more difficult to evaporate and special washer designs may be needed for efficient liquor recovery. When the fuel value of the liquor warrants it, sodium-base sulfite liquors are burned in waterwalled recovery boilers. In other cases, simpler smelters may be used. The sulfide-containing smelt is aggressive toward most refractories, so refractory life can be a

problem. A package recovery boiler for small scale pulp mills consisting of a furnace with gas-tight, water-cooled membrane walls, direct contact evaporator and scrubber has been described. Saturated steam is generated from the water-walls, but there are no convective heat transfer sections to foul or plug. Liquor is concentrated from 25% solids to 60% solids in the direct contact evaporator which serves as the main heat trap.

Most of the reductive recovery systems then separate the sulfur from the sodium by driving it off from the green liquor as H_2S. Carbonation with CO_2 is used to do this. The stripped sulfur is converted to SO_2 and used to sulfite a carbonate solution. Many such processes have been developed and operated.

In the Stora Process, H_2S is stripped from green liquor by CO_2 in a countercurrent stripping tower. The H_2S/CO_2 gas stream is sent to a Claus reactor where it is reacted with SO_2 to form elemental sulfur. The sulfur is burnt to SO_2 for sulfiting and for the Claus reactor. This process is being operated at three mills.

In the Tampella and Rauma Processes, H_2S is steam-stripped from green liquor under conditions which minimize CO_2 release. Upon condensation of the water vapor, the H_2S is burned and converted to SO_2 for sulfiting. Process steps include precarbonation with flue gas and use of concentrated CO_2 to form bicarbonate in a carbonation step separate from H_2S stripping. Recently Tampella obtained rights to the Rauma Recovery Process, and a Tampella-Rauma Process including features from both systems is now available. Versions of this technology have been installed at over 9 mills.

The Farin Process, a modification in which concentrated CO_2 is used under pressure for H_2S removal and bicarbonate decomposition is used as a source

of the pressurized CO_2 has been described. This process has not been piloted or implemented commercially.

The Ebara process operates on a different principle, direct air oxidation of the sulfide to sulfite. Smelt dissolution is carried out in such a manner that a slurry of fine particles is produced. A first stage of oxidation to produce thiosulfate is carried out in this step. Final oxidation to sulfite takes place in contact with a dry powder in a kneader-mixer at a temperature of 150-250°C. This process has been successfully operated at 4 semichemical mills in Japan.

Another direct oxidation process is the RAS process which employs evaporative crystallization to separate carbonate from the green liquor and then converts the sulfide solution to sulfite by air oxidation at 110°C. The sulfite precipitates from the concentrated liquor because of its low solubility and is centrifuged, washed, and dissolved. This has been used at two semichemical mills in Japan.

All of the above approaches involve reductive burning and formation of a Na_2S and Na_2CO_3 smelt. Pyrolysis can be carried out at temperatures below the smelting temperature to achieve a separation of the sulfur from the sodium. This has been implemented commercially in the SCA-Billeruds process in which very rapid heating in a nonoxidizing atmosphere (shock pyrolysis) converts the sodium to a Na_2CO_3 powder and the other liquor constituents into a gas containing most of the sulfur as H_2S. The carbonate powder is separated out and dissolved while the gas is burned with heat recovery. The carbonate solution is then used to scrub the SO_2 out of the flue gas. Supplemental fuel oil is needed to supply the heat for shock pyrolysis. Some unburned carbon is present in the

Na_2CO_3 powder and must be handled. Slag gradually builds up on the walls of the reactor and must be periodically smelted out. This process has been implemented successfully at eight mills.

A novel process which was used for sodium-base sulfite recovery is the Sonoco process in which the spent liquor is mixed with Al_2O_3 and burned in a rotary kiln or ore roasting furnace. The liquor-Al_2O_3 mass is pelletized before being fed to the combustion step. Sulfur is driven off during the burning and is converted to SO_2 in the flue gas. The recovered ash is pulverized, dissolved in water, and used to scrub the SO_2 from the flue gas. This sulfiting step causes Al_2O_3 to precipitate for recycle back to the spent liquor. The mills which were using this process have apparently converted to nonsulfur pulping.

Incineration of sodium sulfite liquors has been used to control pollution problems when a full recovery system could not be justified. Fluidized bed incinerators were most commonly used and the sulfate/carbonate product was sold as a byproduct. Most of the mills which were practicing this have converted to nonsulfur pulping processes. Contamination of the liquor with chloride can cause serious problems with bed fusion, and fluidized bed incineration of chloride-containing liquor is not a practical alternative.

Magnesium-base systems

Magnesium base sulfite pulping is applicable only to bisulfite or acid sulfite pulping because of the limited solubility of the monosulfite. The chemistry of the recovery step is very straightforward. Oxidative burning of the spent liquor converts the magnesium and sulfur to MgO powder and SO_2 gas. Recombination of these materials with water results in the sulfite solution. This provides a basis for a simple recovery technology, but difficulties are encountered due to

the abrasiveness of the MgO, the very low solubilities of the MgO, $Mg(OH)_2$, and $MgSO_3$, and the low concentrations of SO_2 in the flue gas. Magnesium base liquors are also subject to scaling problems during evaporation.

Magnesium based liquors are most commonly burned in suspension at high temperatures and short residence times. The liquor is fired through burners in a refractory-lined combustion chamber at temperatures of 1250-1400°C. The Babcock & Wilcox red liquor furnace and the Lenzing MgO furnace boiler have been used for this purpose. Combustion conditions are regulated to minimize $MgSO_4$ and SO_3 formation and produce a clean ash. The gases pass through the convection section of the boiler, a dust collecter, an air heater and on to the absorber system.

Fluidized bed incinerators have been used for magnesium base liquors. Liquor is sprayed into the top of the reactor at 40-42% solids to maintain autogenous combustion at a temperature of about 930°C in the bed and 1020°C in the freeboard zone. These low temperatures are adequate at the long residence times available in the fluidized bed. The off-gases pass through cyclones to remove MgO dust, a waste heat boiler, a cooler and an absorber.

The SO_2 absorption systems for magnesium base recovery are much more complex than those used with sodium base because of the insolubility of $MgSO_3$ and $Mg(OH)_2$ coupled with the low SO_2 concentrations in the flue gas. Simple countercurrent absorbers are subject to scaling and plugging and specially designed systems must be used. One approach uses three venturi scrubbers in series with incremental amounts of $Mg(OH)_2$ slurry added to each stage under pH control. Tray towers and turbulent contact absorbers with $Mg(OH)_2$ addition

under pH control have also been used. Periodic cleanout of the absorber is required with attendant loss of SO_2.

Ammonium base systems

There is little advantage to ammonium base sulfite over other bases if recovery of the base is contemplated, and ammonium base has mainly been used where easy disposal of the liquor is sought. Incineration of ammonium base liquor will convert the pulping chemicals to gases (N_2 and SO_2). The only ash that needs to be handled in the incinerator is that entering the system with the fiber source being pulped. Concentrated ammonium base liquor burns readily and many different types of incinerators with heat recovery can be used. SO_2 can be scrubbed from the flue gas with an ammonium hydroxide solution if desired. In some cases, ammonium base sulfite liquor from the pulping of agricultural wastes has been used as fertilizer. Such a use is seasonal, and an alternative method is required if the pulp mill is to operate year round.

Calcium-base systems

Calcium base is limited to low pH pulping and does not lend itself to chemical recovery. Calcium sulfite liquors can be concentrated and incinerated and the chemical raw materials (lime and sulfur) are relatively cheap, so incineration and disposal is an option. Historically, calcium sulfite mills have not practiced recovery and they have gradually been phased out as environmental concerns have increased.

Problems With Recovery From Nonwood Pulping

Chemical recovery from nonwood pulping operations is susceptible to special operating problems. These are mostly, but not exclusively, connected to the

high amounts of silica which are introduced into the system with the nonwood fiber source. Inorganic chemical loads tend to be higher. This is partly because the open structure of agricultural residues requires more liquor (unless vapor phase pulping can be practiced) and partly because silica can react with alkali. This means lower organic/inorganic ratios, lower heating values, and more inorganic chemical to be reclaimed and reconverted.

Although adequate pulp washing technology is available in conventional wood pulping, this is not the case for straw pulping. The higher proportion of fines (parenchyma cells), in combination with silica, clog the screens and slow down drainage. Conventional equipment can only be used at much lower efficiencies. There is current interest in horizontal belt washers. In these devices, the pulp slurry is fed by a headbox onto a horizontally driven endless fabric screen while liquor is withdrawn by vacuum boxes. Wash liquid is added at several locations staged for countercurrent washing.

Evaporators are very prone to scaling. The concentrated alkali-silica solution decomposes at the hot surfaces to form siliceous scales. These do not respond to boilout or to chemical treatment and must be mechanically removed. The alkali-silica solution also increases the viscosity of the liquor, lowering heat transfer rates and degrading performance. As a result, maximum liquor solids are limited. Falling-film evaporators and/or forced circulation evaporators may be required, even at low solids contents.

Combustion of high-silica liquors results in the formation of high viscosity silicate glass. This causes formation of "honeycombs" on the boiler wall, plugging of convective boiler passages, difficulties in smelt drainage and impairs combustion. Frequent shutdowns for cleanup are required. In some cases

where problems are severe enough, steam generation from liquor burning is not attempted. Direct contact evaporators in which the hot gases are used to concentrate liquor may provide the only heat recovery.

Silicates in green liquor will react with lime and precipitate as calcium silicate. This interferes with lime mud settling so that mud washing and filtration are more difficult and soda losses are increased. Silica forms glassy silicates in the kiln leading to sticky rings and low efficiency. These problems are usually so severe that lime reburning is not attempted when pulping siliceous fiber sources. Disposal of the lime mud then becomes a problem. Residual sodium in the mud acts to prevent its use as a soil conditioner, even in lime deficient regions.

Desilication Processes

Techniques are available for removing silica from chemical recovery systems. The ideal point for silica removal is from weak black liquor immediately after fiber separation. However, in order to reduce the volume of liquor treated and improve the degree of desilication, partial concentration may be desirable. Desilication can also be carried out on the green liquor. This avoids the interference of the organic compounds in the black liquor, but it doesn't prevent problems in the evaporators or combustion step. There are basically two methods for removal of silica: precipitation by a multivalent cationic material or acidification. Precipitating agents that have been considered include lime, alumina and ferric oxide. Carbonation is the only process used for desilication by acidification.

Lime desilication has received a lot of attention because lime is cheap and calcium silicate is quite insoluble, but no industrially viable process has

emerged. Lime dosages have to be about 6 times the stoichiometric amount needed to form calcium silicate and the filtration properties of the resulting lime mud are unfavorable. Many of these difficulties are lessened with green liquor desilication, but this does not alleviate evaporator or recovery furnace problems.

Alumina has not been found to be effective for removing silica from black liquor. However, when alumina is allowed to react with smelt in the recovery furnace, the aluminum silicate formed is insoluble in green liquor so it can be removed with the green liquor dregs. This has apparently been used successfully at a mill in South Africa. The fate of silica in the presence of ferric oxide during liquor combustion is unclear. This is of considerable importance in light of the potential of the DARS process for simplified recovery for soda process liquor. If silica is converted to a water insoluble form, it would desilicate the liquor but would in turn accumulate in the ferric oxide recycle stream. This could take away one of the main advantages of the DARS process.

CO_2 is the only practical reagent for silica precipitation by partial acidification because of the need to realkalize the liquor to regain lignin stability. Under proper conditions it is possible to precipitate silica without precipitating lignin. The critical pH limit must be established for each liquor. As the pH drops sodium bicarbonate is formed and silica precipitates according to the reaction,

$$Na_2SiO_3 + H_2O + 2\ CO_2 = 2\ NaHCO_3 + SiO_2$$

In practice, carbonation is carried out at higher temperatures, in spite of the fact that silica solubility increases with increasing temperature, to conserve the heat in the black liquor. It is critically important to obtain the silica

in a flocculated, easily filterable form, but this is not necessarily straightforward.

Recently, a pilot trial of desilication of rice straw black liquor was described. Partially concentrated black liquor at 8-14% solids was reacted with flue gas to drop the pH to between 9 and 10. The carbonated liquor was sent to a decanter to separate the precipitate from the clean liquor, and the filtrate was passed through a centrifugal separator before being further concentrated in the evaporation plant. The precipitated silica, along with some alkali and organic matter, forms a sludge which is discharged at 30-40% solids and burned in a fuel-oil-fired incinerator. The alkali content of the ash can be eluted with water, and the resulting silica can be used as a papermaking filler. Desilication efficiencies of 95% were claimed.

Biological Processes

Biological processes may play an increasingly important role in recovery for high yield pulping processes, particularly for small mills. They can be carried out on low concentration liquors and avoid the problems connected with evaporation. The objective of most of the biological processes has been the destruction of organic matter to reduce the BOD or COD demand so that the effluent can be disposed of. More recently, combined anaerobic/aerobic processes have come into use that produce biogas that conserve the fuel value of the liquor organics and leave an inorganic-rich liquid phase that can be processed further. Since the pH drops during the biological step, it is conceivable that a biological process could provide acidic desilication in conjunction with biogas production.

The ANAMET anaerobic-aerobic process has been operated at several pulp mills treating effluent from TMP production, the total wastewater from a

soda-based semichemical corrugating medium mill, and sulfite evaporator condensate. The wastewater at the 225,000 t/y corrugating medium mill is a combination of the spent pulping liquor and papermachine whitewater. The ANAMET plant has achieved COD and BOD reductions of 67 and 97%, respectively. Average biogas production corresponds to the heat value of 13 tons of oil per day.

Summary

Kraft recovery technology is the most advanced, but is not generally suited to small nonwood pulping operations. Sulfite recovery technology is also generally too complex for these types of operations. Sulfur-free soda pulping would provide the best opportunity for relatively simple recovery technologies. The DARS process may provide a very attractive chemical recovery system for the small soda mill. Its applicability to nonwood pulping depends on the behavior of silica in the combustion step. There remains a need for a simple and reliable method for desilicating black liquor. This is the key to effective recovery for alkaline nonwood pulping. Continued development of biological processes may provide some longer range solutions for small nonwood pulping chemical recovery.

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